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ON THE MECHANISM OF THE OXIDATION OF NAPHTHALENE. II.

THE COURSE OF THE OXIDATION OF β-NAPHTHOQUINONE TO PHTHALIC ACID

BY MAITLAND C. BOSWELL.

In many of the reactions of organic chemistry, where the ultimate product is only distantly related to the substances initially present, it is of great interest to trace the intermediate steps of the reaction; either, for example, to elucidate some theory as that of ring opening in the oxidation of cyclic compound or in the hope of discovering constitutional formulas for, and ultimately achieving the synthesis of, the substances experimented on.

Up to the present, information as to the course of such reactions has been sought by examining the reaction product for the intermediate compound suspected, and by varying the conditions of the reaction, such as temperature and concentrations, by exchanging one oxidizing or reduction agent for another, by adding alkali or acid, to discover, if possible, conditions under which they would be formed in isolable quantities. Much has been accomplished in this manner.

There is, however, a second method of procedure which is illustrated by the experiments of the present paper, and which, so far as I am aware, has not hitherto been put in practice. This consists in studying the behavior of the suspected intermediate products with the reagents used in the reaction in question, in order to see whether, if formed, they would accumulate in the reaction mixture or would be converted at once into the final product.

This second method is, in a sense, a check on the first; each furnishes information that the other cannot. Failure to isolate any particular substance cannot be regarded as proof that it did not exist temporarily at some stage of the reaction; and on the other hand, proof that the substance in question could not remain

presence of the reagents, is proof merely that it might have been not that it actually was formed as an intermediate stage of the reaction.

The first method, then, may lead to positive evidence that a given substance is one of the intermediate products of the reaction, the second, to positive evidence that it is not. Neither method can furnish evidence of the kind peculiar to the other.

A few simple experiments carried out by either of the two methods may often give valuable information; but to obtain really conclusive evidence by either of them, all the precautions suggested by the study of chemical kinetics must be observed. In applying the first method, in particular, it has too often been forgotten that change of conditions often entails a radical change in the mechanism of the reaction. An example of such a change is afforded by my experiments on the oxidation of β naphthoquinone, discussed on page 127.

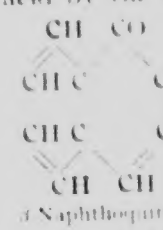
In a paper which has just been published, Mr. Daly[1] has made a careful study of some of the likely intermediate stages in the formation of phthalonic acid by the action of potassium permanganate on naphthalene. The present experiments with β naphthoquinone and some of its possible oxidation products show how, under favorable circumstances, a few simple measurements may lead to equally definite results.

In the oxidation of β naphthoquinone to phthalic acid,[2] the ring may be broken at the double bond, between the two keto groups, or between the CO and CH groups; of these the last named seems the least likely, from chemical analogies, while simultaneous dissolution of two or more bonds is least likely of all.

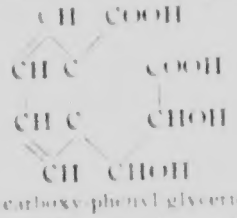
The first alternative would result in the formation of carboxy phenylglyoxyl formic acid, which on further oxidation might be converted into phthalonic acid and then into phthalic acid (Series A). The experiments of Zincke[3] and of

[1] Jour. Phys. Chem., **11**, 93 (1907).
[2] Liebig's Ann., **189**, 155 (1877).
[3] Ber. chem. Ges., Berlin, **25**, 400 (1892).

Ba...erger and Kitschelt,[1] who prepared ortho carboxy phenyl glyceric acid by the action of chloride of lime on β naphtho



β Naphthoquinone

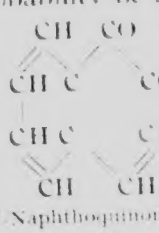


Ortho carboxy phenyl glyceric acid

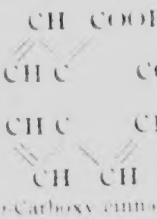
quinone, lend probability to the second supposition (Series II), and I have accordingly undertaken experiments to ascertain whether the oxidation by chromic acid follows the same course.

The first product of the oxidation, if the bond between the two keto groups be broken, would be *o* carboxy cinnamic acid. I do not find in the literature any account of this substance having been oxidized without loss of carbon, but cinnamic acid itself gives phenylglyceric acid,[2] *o* carboxy phenylglyceric acid may therefore be assumed with perhaps *o* carboxy benzoylacetic acid (the hydrate of phthalylacetic acid) intermediate. Homophthalic acid, and carboxy mandelic acid (the hydrate of phthalid carbonic acid), both of which may be obtained from phthalonic acid by reduction, may also reasonably be regarded as possible stages in the oxidation, since my own experiments show that phthalonic acid is actually formed from each of them.

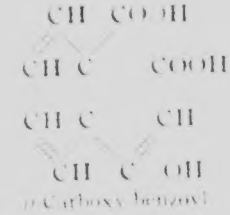
The steps by which β naphthoquinone is oxidized to phthalic acid, on the assumption that the bond between the two CO groups is the first to break, may thus with some probability be assumed to be



β Naphthoquinone



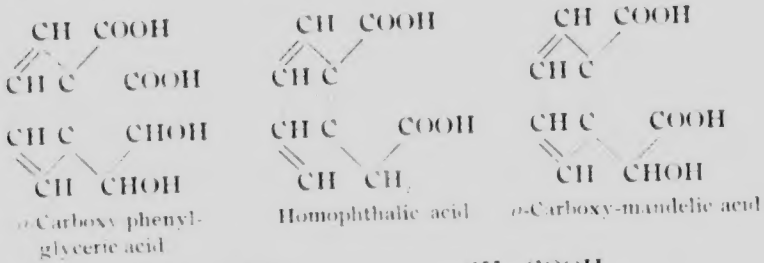
o Carboxy cinnamic acid

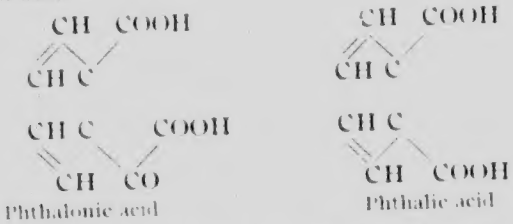


o Carboxy benzoyl acetic acid

[1] Ber. chem. Ges., 25, 888 (1892).

[2] Fittig, Liebig's Ann., 268, 27 (1892).





Substances Used in the Experiments

β Naphthoquinone, prepared by the method of Lagodzinski and Hardline[1] and purified by the method described in my paper on "Analytical Methods."[2]

The lactone of ortho-carboxy-phenylglyceric acid, by the method of Zincke;[3] melting point 202°.

Ortho-carboxy-cinnamic acid, by the method of Ehrlich and Benedikt.[4]

Phthalyl-acetic acid, by the method of Gabriel and Neumann.[5]

Homophthalic acid, by the method of Graebe and Trümpy,[6] melting-point 174°–175°.

The lactone of phthalid-carbonic acid, by the method of Graebe and Trumpy,[7] melting point 150°–152°.

Phthalonic acid, by the method of Graebe and Trumpy.[8] As I found that air dried phthalonic acid does not contain a

[1] Ber. chem. Ges., Berlin, **27**, 3075 (1894).
[2] Jour. Am. Chem. Soc., **29**, 230 (1907).
[3] Ber. chem. Ges., Berlin, **25**, 405 (1892).
[4] Monatsheft. **9**, 528 (1888).
[5] Ber. chem. Ges., Berlin, **26**, 952 (1893).
[6] Ibid., **31**, 375 (1898).
[7] Ibid., **31**, 373 (1898).
[8] Ibid., **31**, 369 (1898).

definite amount of water of crystallization,[1] I used anhydrous acid which I prepared by heating the air-dried acid at 115° to constant weight.

α-Naphthoquinone, by the method of Japp and Miller[2] and purified by repeated crystallization from petroleum ether, melting point 124° 126°.

The α-naphthol and the naphthalene were "chemically pure" preparations of Kahlbaum.

Method of Working

The rates of oxidation were measured as follows. In a 150 cc glass-stoppered bottle was placed 0.1000 gram naphthoquinone (or an amount of one of the other substances proportional to its formula weight); and a mixture of 70 cc of potassium bichromate solution (7.648 grams $K_2Cr_2O_7$ per liter) with 5 cc of dilute sulphuric acid (150 grams H_2SO_4 per liter) was added. The bottle was completely immersed in a bath of boiling water, at the expiration of a measured interval it was removed, emptied into a beaker containing 75 cc ice-water and titrated with approximately fortieth-normal ferrous sulphate, using potassium ferricyanide as external indicator in the usual way. The results of the measurements are contained in Table I.

In the first column are the names of the substances, in the second the formulas, in the third the weights taken, in the fourth, after the duration of the oxidation in minutes, and after *B*, the amount of bichromate reduced, expressed in cc of a *solution* containing 7.648 grams $K_2Cr_2O_7$ per liter. In the fifth column, under *I*, are entered the number of cc of bichromate (calculated from the formulas) necessary to oxidize the substance to phthalonic acid, and under *t* the number of minutes (obtained graphically from the data of the table) in which these quantities of bichromate are reduced.

Of course, it cannot be assumed that at the moment *t* nothing but phthalonic acid is present in the solution, for that

[1] Jour. Am. Chem. Soc., **29**, 230 (1907).

[2] Jour. Chem. Soc., **39**, 220 (1881).

TABLE I

Substance	Formula	Weight taken Gram		Results of the Measurements								P	T
β-Naphtho quinone	$C_{10}H_6O_2$	0.1000	t	2.5	5	10	20	40	80	150	210		
			Bt	4.4	14.4	21.6	27.3	31.6	37.7	41.5	45.7	40.5	128
Ortho carboxy-cinnamic acid	$C_{10}H_8O_4$	0.1215	t	30		60	90		120	150	180		
			Bt	9.1		12.7	18.8		19.3	21.5	21.2	32.4	250
Ortho carboxy-phenylglyceric acid (Lactone)	$C_{10}H_8O_5$	0.1317	t	30		60	90		120	150	180		
			Bt	1.2		5.0	9.5		12.8	17.8	21.9	24.3	200
Phthalyl acetic acid	$C_{10}H_8O_4$	0.1203	t	30		60	90		120	150	200		
			Bt	8.5		12.7	15.1		17.2	20.6	24.6	24.3	200
Homophthalic acid	$C_9H_8O_4$	0.1140	t	30		90	120						over
			Bt	0.5		1.2	1.9					16.2	1000
Phthalid-carbonic acid (Lactone)	$C_9H_6O_4$	0.1130	t	30		60	90		120				
			Bt	1.5		3.6	5.1		6.9			8.1	160
Phthalonic acid (anhydrous)	$C_9H_6O_5$	0.1230	t	40		80	140						
			Bt	8.2		10.2	16.9					0	0
Phthalic acid	$C_8H_6O_4$	0.1050	t	30		60	90						
			Bt	1.0		3.0	6.0					—	—

substance itself is oxidized by chromic acid. This reaction, however, takes place slowly in the relatively dilute solution of chromic acid left by the previous oxidation, as is shown by the measurements of Table II.

TABLE II

Phthalonic acid Gram	Bichromate cc.	Sulphuric acid cc.	t minutes	Bi cc.
0.1230	70	5	40	8.2
0.1230	70	5	80	10.2
0.0615	70	5	40	2.7
0.0615	70	5	80	4.4
0.1230	35	5	40	6.0
0.1230	35	5	80	8.0
0.1230	70	2.5	40	0.3
0.1230	70	2.5	80	7.0

The weights of anhydrous phthalonic acid taken are entered under *Phthalonic acid*, the volumes of the bichromate solution and of the acid (page 123) under *Bichromate* and *Sulphuric acid* respectively, the duration of the oxidation under *t*, and the bichromate reduced under *Bi*. The great effect of the concentrations of the reagents on the rate is sufficiently obvious. From a graph of the results it appears that the rate is proportional to the concentrations of the sulphuric acid and of the bichromate respectively, and to the square of that of the phthalonic acid; but for the purposes of this paper it was not necessary to undertake special measurement to establish this relation rigorously.

Far the greater part of the phthalonic acid formed in my experiments would thus escape further oxidation, and, in fact, the presence of that substance in each of the solutions at the expiration of *t* minutes was established by the test with potassium permanganate described in my paper on "Analytical Methods."[1] This test was carried out as follows. First, the chromic acid remaining was reduced with ferrous sulphate. The phthalonic acid

[1] *loc. cit.*

was then isolated by neutralizing with sodium carbonate, acidifying with hydrochloric acid, evaporating to dryness on the water-bath, extracting with absolute alcohol and evaporating the alcoholic extract to dryness; the residue was then dissolved in a little water and filtered. The solution so obtained was acidified with dilute sulphuric acid, and deci normal permanganate was added; in every case the color was discharged, a reaction characteristic of phthalonic acid and serving to distinguish it from phthalic, homophthalic and phthalid-carbonic acids

Phthalonic acid is thus an isolable product of the oxidation of all six substances studied, similar experiments showed that it is formed by the oxidation of α naphthoquinone; hitherto it has been known as a product of oxidation of naphthalene[1] and of α-naphthol[2] only

I

β-Naphthoquinone

A glance at Table I shows that the number entered under *I* opposite β naphthoquinone is the smallest in the column. In other words, 0.1000 gram of the quinone is oxidized to phthalonic acid in less time than it would take to oxidize any of the hypothetical intermediate oxidation products of Series B (page 124), even if they had been present in full concentration and had the chromic acid all to themselves

This shows conclusively that neither orthocarboxy cinnamic, ortho carboxy-phenylglycerie, phthalyl acetic, homo phthalic, nor phthalid-carbonic acid can be formed in the course of the oxidation of β naphthoquinone to phthalic acid, and, as has been pointed out in the introduction, positive evidence of this nature can be obtained in no other way. That phthalonic acid is an intermediate product is shown by the permanganate test described above

The measurements with α carboxy phenylglycerie acid

[1] Fischer: Ber. chem. Ges., Berlin, **31**, 139 (1898); Graebe and Trumpy: Ibid., **31**, 377 (1898)

[2] Henriques: Ibid., **21**, 1007 (1888)

are particularly interesting, because the very preparation of this substance used in my measurements was itself made from β-naphthoquinone by the action of chloride of lime. There was therefore, *a priori*, a high degree of probability that it would prove to be one of the products of oxidation with chromic acid. Changing the oxidizing agent, however, has changed the whole course of the oxidation.

The experimental study of Series *A* was prevented by the circumstance that carboxy-phenylglyoxyl-formic acid has not yet been described in the literature, and that as yet I have had no leisure to attempt its preparation. In the present almost total absence of data of the kinetics of organic reactions, it is impossible to draw from its formula any sure conclusions as to its behavior on oxidation. The analogous phenylglyoxyl-formic acid, or rather an amino derivative of it, has been prepared by Baeyer and Homolka,[1] but nothing is said as to its behavior with oxidizing agents; similarly, nothing could be found as to the oxidation of dioxytartaric acid, or diphenyltriketone, both of which likewise contain the group CO.CO.CO. The result of my measurements, then, while conclusively disproving the possibility of the mecha- represented by the formulas of Series *B* leaves the ques-ion open as to Series *A*

II

Genetic Relations between the Six Acids

From the data of Table I, collected in order to study the oxidation of β naphthoquinone, some information as to the relations of the acids involved may be drawn It is immediately obvious for instance, that homophthalic acid cannot be an intermediate product of the oxidation of either orthocarboxy-cinnamic, orthocarboxy phenylglyceric, or phthalyl-acetic acids to phthalonic acid. Without further study of the relations between rates and concentrations, which (as aside from the main purpose of the research was

[1] Ber. chem. Ges. Berlin, 16, 2219–88

not undertaken, nothing further definite can be said, but if the plausible assumption be allowed, that in each case the rate is proportional to at least the first power of the concentration of the acids oxidized, then none of the acids studied can be considered as intermediate stages in the oxidation to phthalonic acid of those higher in the Table

III

α Naphthoquinone

In this connection, a few experiments were conducted with α naphthoquinone, the results of which are given in Table III

TABLE III

α Quinone taken Gram	Results of the Measurements						P	T
0.1000	t	30	60	90	120	150	180		
	B	5.1	11.6	20.8	26.2	31.6	35.6	40.5	220

Taken with the data of Table I these measurements show that orthocarboxy cinnamic and homophthalic acids cannot be intermediate products in the oxidation of α naphthoquinone to phthalonic acid under the circumstances of my experiments. Without further measurements to ascertain the effect of concentrations on the rates the same cannot be said of orthocarboxy phenylglyceric and phthalid-carbonic acids Consideration of the structural formulas, however, makes it very unlikely. It is possible, however, to show from the data of Tables I and III that phthalyl-acetic acid cannot be an intermediate product.

40.5 cc bichromate are necessary to transform 0.1 gram of α quinone into phthalonic acid and need 220 minutes to do it. 16.2 cc bichromate would be necessary to oxidize the quinone to phthalyl, acetic acid, and the table shows that this amount of bichromate is reduced in 77 minutes. Experiments on the rate of oxidation of phthalyl-acetic acid show (by interpolation) that in the last 22 – 077 – 143 minutes at most 0.51 equivalent[1]

[1] By one "equivalent" is to be understood the weight of substance entered in column 3 of Table I

of that substance could be oxidized, leaving at least 0.49 equivalent that must have been oxidized in the first 7" minutes. This oxidation would require 0.49 × 24.3 = 11.9 cc of bichromate out of the 16.2 actually reduced, leaving only 4.3 reduced by the quinone. The phthalylacetic acid formed by the reduction of this amount of bichromate, however, amounts to only 4.3 : 16.2 = 0.26 equivalent instead of the minimum of 0.49 required by the assumptions.

The assumption that phthalylacetic acid is an intermediate product of the oxidation of α-naphthoquinone to phthalonic acid is therefore disproved by the rate measurements.

The same process of reasoning makes it most improbable that phthalid-carbonic acid can be intermediate in the oxidation of orthocarboxy-cinnamic acid to phthalonic acid.

IV

α-Naphthol

The results of a series of experiments with α-naphthol given in Table IV show that homophthalic acid cannot be formed "on the way" to phthalonic acid, so far as my experiments go, however, any of the other six compounds studied may be intermediate compounds.

TABLE IV

α-Naphthol taken: Gram	Results of the Measurements						
0.0951	t	30"	60"	90"	15'	180'	
	cc Br	18.6	20.1	25.1	29.7	29.7	56.7

V

The Action of Nitric Acid on Naphthalene

Laurent[1] and Beilstein[2] have shown that phthalic acid can be prepared by the action of nitric acid (sp. gr. 1.15) on naphthalene, and the latter even stated that "apart from the trouble of working in sealed tubes this is the cheapest way of

[1] Liebig's Ann., 19, 58 (1836).
[2] Ibid., 202, 215 (1880).

preparing this substance." I undertook a long series of measurements in the hope of ascertaining the mechanism of this reaction but without success, as in all my experiments — whether carried out in tubes or in open vessels — large quantities of nitro compounds were formed, and conditions could not be found under which oxidation took place anything like quantitatively.

The following table gives the results of a series of determinations of the phthalic acid produced by the action of 40 cc of nitric acid (sp. gr. 1.15) in six hours at 100° on naphthalene, α- and β naphthoquinones, homophthalic, and phthalid-carbonic acids.

TABLE V

Substance	Weight taken	Phthalic acid formed
Naphthalene	2.0000	0.076
"	2.0000	0.074
α naphthoquinone	0.0712	0.057
"	0.0712	0.045
β naphthoquinone	0.0712	0.043
"	0.0712	0.038
Homophthalic acid	0.0814	0.036
"	0.0814	0.047
Phthalid carbonic acid	0.0804	0.041
"	0.0804	0.041

SUMMARY

The method of determining the course of an organic reaction discussed in this paper is complementary to the method of isolation of intermediate compounds heretofore exclusively employed. It is shown that under favorable circumstances simple measurements may quickly lead to definite conclusions.

In the case of the oxidation of β-naphthoquinone to phthalic acid, phthalonic acid is an intermediate product, while o-carboxy-cinnamic, o-carboxy-phenylglyceric, phthalyl acetic, homophthalic, and phthalid carbonic acids are not.

Homophthalic acid is not an intermediate product in the oxidation of any of the other acids named, of α-naphthoquinone, or of α-naphthol.

o-Carboxy cinnamic and phthalyl acetic acids are not intermediate products in the oxidation of α naphthoquinone.

These conclusions hold only for chromic acid as oxidizing agent; changing the oxidizing agent may change the whole course of the reaction.

My thanks are due to Prof. Lash Miller, at whose suggestion this research was undertaken.

The University of Toronto,
December, 1906.